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TUNABLE VACUUM ULTRAVIOLET-LASER SPECTROSCOPY OF THE D(O-U(+)) ION-PAIR STATE OF JET-COOLED I₂

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Tunable vacuum ultraviolet laser spectroscopy of the D(O+u) ionpair state of jetcooled I₂

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Tunable vacuum ultraviolet laser spectroscopy of the $D(O_u^+)$ ion-pair state of jet-cooled I_2

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High-resolution vacuum ultraviolet fluorescence excitation spectra of the $D(O_u^+)$ ion-pair state of I_2 have been obtained using a pulsed supersonic jet. Tunable vacuum ultraviolet radiation in the region 184–200 nm was produced by Raman shifting (fifth and sixth anti-Stokes) the output from a tunable excimer pumped dye laser. Vibrational constants valid up to $v' = 201$ in the $D(O_u^+)$ state have been determined.

I. INTRODUCTION

The vacuum ultraviolet (VUV) absorption spectrum of I_2 has been studied for 60 years.^{1–4} Between 176 and 200 nm it shows a broadband system, the so-called Cordes bands. This band system has been assigned as the transition from the $X(O_g^+)$ ground state to the $D(O_u^+)$ ion-pair state which, although initially believed to be in the second cluster of ion-pair states,⁵ is now known to belong to the lowest cluster. Fluorescence back to the ground state is recorded as a highly structured continuum (McLennan bands) between ~250 nm and 330 nm and as a discrete region below 250 nm.^{6–10} Emission to the repulsive $a'(O_g^+)$ state has also been reported by Lawley *et al.*¹¹

The broad system between 176 and 200 nm observed in the absorption and fluorescence excitation spectra can be partially resolved into a long series of vibrational bands separated by 40–60 cm^{-1} . Because of the characteristically large equilibrium bond lengths of the ion-pair states in the halogens, Franck–Condon factors dictate that high vibrational levels in the D state are excited (levels well above $v' = 100$) following single-photon excitation from the ground state. The optical-optical double-resonance (OODR) technique has been used to access low-lying vibrational levels ($v = 0–124$) of the D state in a $1 + 2$ photon OODR experiment using the $B(O_u^+)$ state as the intermediate state.^{12,13}

In this study we have used the Raman-shifted output from an excimer pumped dye laser to achieve single-photon excitation of the D ion-pair state of I_2 . Using a pulsed supersonic jet (rotational temperature ~10 K) the congested fluorescence excitation spectrum observed at room temperature has been greatly simplified.

II. EXPERIMENTAL

The experimental setup is shown in Fig. 1. An excimer pumped dye laser (Lambda Physik EMG201MSC/FL3002E) was combined with a Raman shifter (Lambda Physik RS75) to produce tunable VUV radiation. The Ra-

man shifter consisted of a high-pressure cell, which for fifth and sixth anti-Stokes generation was filled with hydrogen at an optimum pressure of 3 bar. This contrasts with the optimum pressure of 16 bar reported by Baldwin *et al.*¹⁴ when using a similar pumping scheme. Tunable VUV radiation was generated in the region 184–201 nm using the sixth anti-Stokes lines from the output of the dyes PTP, DMQ, and QUI and the fifth anti-Stokes line from PTP. The absolute energy output on these lines was not measured, but it should be of the order of 10^{-5} J (dye laser energy 20–30 mJ, conversion efficiency $\sim 10^{-3}$).¹⁵ The linewidth is expected to be of the order of the dye laser linewidth (~ 0.3 cm^{-1})¹⁶ and our data support this. A Pellin–Broca prism was used for separation of the Raman shifted lines, and the appropriate line was directed via an iris aperture into the molecular-beam vacuum chamber. Tuning of the laser wavelength resulted in spatial movement of the wavelength-dispersed output from the Raman shifter such that only ~ 500 cm^{-1} scans could be achieved before realignment of the chosen anti-Stokes line with respect to the aperture was necessary. The beam path between the hydrogen cell and the vacuum chamber was purged with nitrogen to minimize oxygen absorption.

The pulsed supersonic jet was produced by an automobile fuel-injector valve (Toyota, orifice diameter 0.5 mm),¹⁷ mounted on an X, Y, Z translator, operated at 5 Hz with a pulse width of ~0.8 ms. The I_2 sample was contained in an

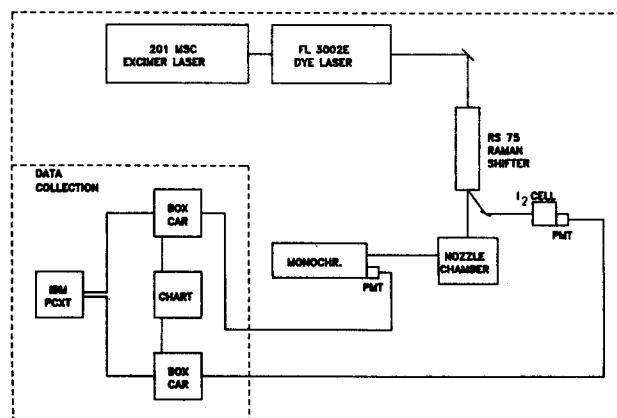


FIG. 1. Schematic diagram of the experimental apparatus.

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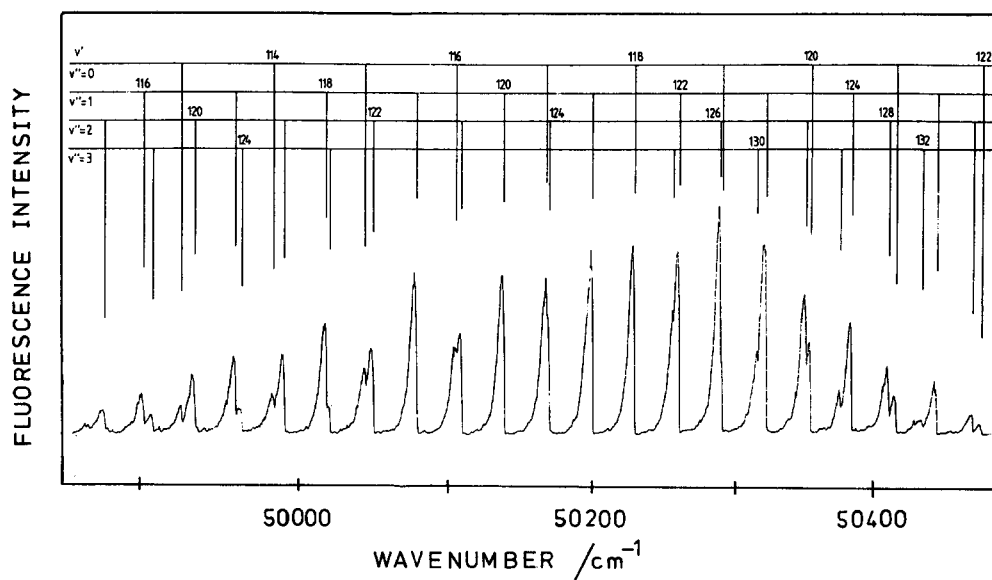


FIG. 2. $D \leftarrow X$ fluorescence excitation spectrum of jet-cooled I_2 recorded using the fifth anti-Stokes Raman-shifted output of PTP dye and a backing pressure of 1.5 bar of helium.

in-line filter which could be heated to temperatures as high as 400 K to increase the vapor pressure. The heater (Philips thermocoax) covered both the filter and the nozzle. He or Ar was used as the carrier gas at pressures up to 3 bar and the background pressure in the vacuum chamber was maintained below 10^{-3} mbar. The expanding jet was crossed 10 mm from the nozzle orifice by the appropriate anti-Stokes line from the Raman shifter.

Fluorescence was collected at right angles using a monochromator (McKee-Pederson 1018B), detected by a photomultiplier (Hamamatsu R928), processed by a boxcar integrator (SRS250), and recorded either on a chart recorder or computer (IBM XT). Excitation spectra were recorded by setting the monochromator to the head of the I_2 ($D \leftarrow X$) oscillatory continuum (322 nm) with 6 mm slits providing a bandpass of 10 nm. No attempts were made to correct the spectra for the energy profile of the exciting radiation. In order to calibrate the spectra, the I_2 ($B \leftarrow X$) fluorescence excitation spectrum (500–600 nm), excited in a static cell by the appropriate second or third Stokes line, was recorded simultaneously, collecting the total fluorescence via a cutoff filter (Hoya R-64). Absolute wave numbers were taken from an I_2 atlas,¹⁸ with the Raman shift in 3 bar of hydrogen taken to be 4155.250 cm^{-1} .^{19,20} The resultant errors in the vibronic band positions are estimated to be $\sim 0.5 \text{ cm}^{-1}$.

III. RESULTS AND DISCUSSION

A. Spectra recorded at vibronic resolution

Figure 2 shows a fluorescence excitation spectrum for the $D \leftarrow X$ transition recorded between 198.1 and 200.6 nm using the fifth anti-Stokes line from the dye PTP, under medium free jet expansion conditions (1.5 bar He backing pressure). The spacing between the major bands is $\sim 30 \text{ cm}^{-1}$, which is only half the expected vibrational spacing for the D ion-pair state around $v' = 120$. This is because every second main band is due to absorption from $v'' = 1$ of the ground state. The peaks which lie very close to bands originating from $v'' = 0$ and $v'' = 1$ can be assigned as excitation from

$v'' = 2$ and $v'' = 3$ of the ground state. Spectra showing some of these bands were recorded with different backing pressures (see Fig. 3) in order to assign the lower state vibrational levels. As the backing pressure is increased the vibrational

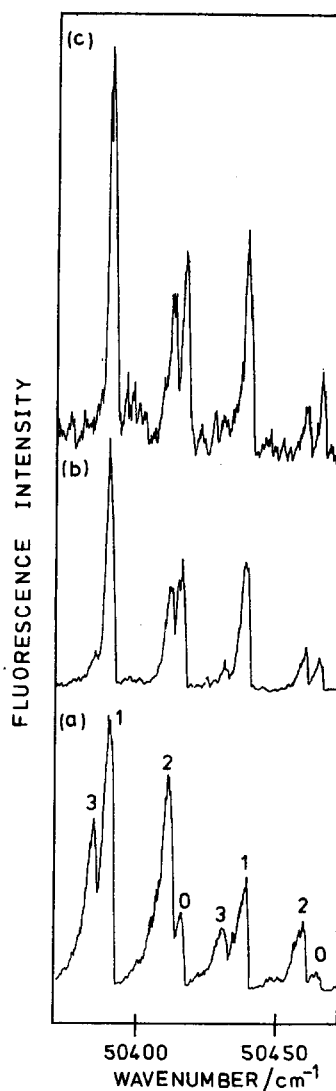


FIG. 3. $D \leftarrow X$ fluorescence excitation spectrum of jet-cooled I_2 recorded with backing pressures of (a) 1.2, (b) 2.0, and (c) 3.0 bar of helium. The v'' levels involved in the transitions are indicated.

temperature decreases and bands due to excitation from $v'' = 0$ and $v'' = 1$ begin to dominate the spectrum. Similarly, transitions from $v'' = 0$ can be distinguished from those with $v'' = 1$.

In Table I the positions of the bandheads are presented. As noted earlier, the equilibrium bondlengths of the ion-pair states are longer than that of the ground state. Thus, the rotational constants for the D state will be considerably

TABLE I. Transition wave numbers and vibrational assignment for the $D(O_u^+) - X(O_g^+)$ transition of I₂.

v'	v''	$\tilde{\nu}$ (cm ⁻¹)	v'	v''	$\tilde{\nu}$ (cm ⁻¹)	v'	v''	$\tilde{\nu}$ (cm ⁻¹)
113	0	49 916.6 (0.4) ^a	144	0	51 748.2 (0.2)	175	0	53 357.8 (0.2)
114	0	49 979.3 (0.2)	145	0	51 802.6 (−0.7)	176	0	53 406.3 (0.1)
115	0	50 041.6 (−0.1)	146	0	51 858.0 (−0.2)	177	0	53 454.4 (−0.2)
116	0	50 104.2 (0.1)	147	0	51 913.1 (0.1)	178	0	53 502.2 (−0.6)
117	0	50 166.5 (0.3)	148	0	51 967.8 (0.3)	179	0	53 550.8 (−0.1)
118	0	50 227.9 (0.1)	149	0	52 021.8 (0.0)	180	0	53 598.7 (0.0)
119	0	50 289.5 (−0.1)	150	0	52 076.1 (0.2)	181	0	53 646.6 (0.3)
120	0	50 351.0 (0.1)	151	0	52 129.9 (0.1)	182	0	53 693.8 (0.0)
121	0	50 412.1 (0.1)	152	0	52 183.4 (0.0)	183	0	53 741.2 (0.2)
122	0	50 472.9 (0.1)	153	0	52 236.5 (−0.3)	184	0	53 788.0 (−0.1)
123	0	50 533.9 (0.6)	154	0	52 289.3 (−0.7)	185	0	53 835.5 (0.6)
124	0	50 593.8 (0.1)	155	0	52 343.2 (0.3)	186	0	53 881.7 (0.0)
125	0	50 653.7 (0.0)	156	0	52 395.7 (0.0)	187	0	53 928.5 (0.2)
126	0	50 713.4 (−0.1)	157	0	52 448.2 (0.0)	188	0	53 974.8 (0.0)
127	0	50 773.3 (0.2)	158	0	52 500.5 (0.0)	189	0	54 020.8 (0.0)
128	0	50 832.5 (0.1)	159	0	52 552.5 (−0.1)	190	0	54 067.2 (0.4)
129	0	50 891.8 (0.4)	160	0	52 603.9 (−0.6)	191	0	54 112.9 (0.3)
130	0	50 950.6 (0.4)	161	0	52 656.2 (−0.1)	192	0	54 158.3 (0.1)
131	0	51 009.4 (0.6)	162	0	52 707.9 (0.3)	193	0	54 203.5 (−0.2)
132	0	51 067.6 (0.5)	163	0	52 758.5 (−0.3)	194	0	54 249.1 (0.1)
133	0	51 125.8 (0.7)	164	0	52 810.0 (0.1)	195	0	54 294.1 (0.0)
134	0	51 183.3 (0.3)	165	0	52 860.8 (0.1)	196	0	54 339.1 (0.0)
135	0	51 240.6 (0.1)	166	0	52 910.8 (−0.5)	197	0	54 383.7 (−0.2)
136	0	51 297.9 (0.0)	167	0	52 961.6 (−0.1)	198	0	54 428.7 (0.2)
137	0	51 355.4 (0.4)	168	0	53 011.9 (0.0)	199	0	54 473.1 (0.1)
138	0	51 411.9 (0.1)	169	0	53 061.6 (−0.3)	200	0	54 517.2 (−0.1)
139	0	51 468.8 (0.3)	170	0	53 112.0 (0.3)	201	0	54 561.2 (−0.5)
140	0	51 525.0 (0.2)	171	0	53 161.5 (0.2)	116	1	49 890.4 (−0.4)
141	0	51 581.3 (0.3)	172	0	53 210.7 (0.0)	117	1	49 952.9 (0.0)
142	0	51 637.4 (0.5)	173	0	53 259.5 (−0.3)	118	1	50 014.7 (0.0)
143	0	51 692.7 (0.1)	174	0	53 308.8 (0.0)	119	1	50 076.5 (0.2)
120	1	50 137.6 (0.0)	151	1	51 915.6 (−0.9)	129	2	50 466.3 (0.3)
121	1	50 198.8 (0.1)	157	1	52 234.3 (−0.6)	130	2	50 524.8 (0.0)
122	1	50 259.4 (−0.1)	158	1	52 287.2 (0.0)	131	2	50 583.1 (−0.3)
123	1	50 320.0 (0.0)	159	1	52 339.5 (0.2)	132	2	50 641.4 (−0.3)
124	1	50 380.1 (−0.3)	160	1	52 390.7 (−0.5)	133	2	50 699.8 (0.1)
125	1	50 440.7 (0.3)	162	1	52 494.4 (0.1)	134	2	50 757.6 (0.0)
126	1	50 500.3 (0.1)	163	1	52 545.6 (0.1)	135	2	50 815.3 (0.2)
127	1	50 559.8 (0.0)	164	1	52 596.4 (−0.3)	136	2	50 871.4 (−1.1)
128	1	50 619.2 (0.1)	165	1	52 647.5 (0.1)	137	2	50 930.0 (0.4)
129	1	50 678.3 (0.2)	166	1	52 698.1 (0.1)	138	2	50 986.3 (−0.1)
130	1	50 737.3 (−0.6)	167	1	52 748.4 (0.0)	139	2	51 042.8 (−0.3)
131	1	50 795.7 (0.2)	168	1	52 798.6 (0.0)	140	2	51 099.4 (0.0)
132	1	50 854.0 (0.2)	169	1	52 848.5 (−0.1)	141	2	51 156.2 (0.6)
133	1	50 911.7 (−0.1)	170	1	52 898.2 (−0.2)	143	2	51 267.3 (0.1)
135	1	51 027.3 (0.1)	171	1	52 948.0 (0.0)	144	2	51 322.0 (−0.6)
136	1	51 084.9 (0.3)	172	1	52 997.2 (−0.2)	145	2	51 376.4 (−1.5)
137	1	51 142.3 (0.6)	175	1	53 144.1 (−0.2)	146	2	51 432.9 (0.1)
138	1	51 199.0 (0.5)	176	1	53 193.0 (0.1)	147	2	51 487.8 (0.2)
139	1	51 255.1 (−0.1)	177	1	53 241.6 (0.3)	148	2	51 542.2 (0.1)
140	1	51 311.1 (−0.4)	178	1	53 289.3 (−0.2)	122	3	49 836.4 (−0.2)
141	1	51 367.8 (0.1)	119	2	49 864.0 (−0.2)	123	3	49 896.6 (−0.5)
142	1	51 423.7 (0.1)	120	2	49 925.2 (−0.3)	124	3	49 957.1 (−0.4)
143	1	51 480.3 (1.0)	121	2	49 986.8 (0.2)	125	3	50 017.4 (−0.1)
144	1	51 535.2 (0.5)	122	2	50 047.4 (0.0)	126	3	50 077.2 (−0.1)
145	1	51 590.2 (0.2)	123	2	50 108.0 (0.1)	127	3	50 136.9 (0.0)
146	1	51 645.4 (0.5)	124	2	50 168.4 (0.1)	128	3	50 196.3 (0.1)
147	1	51 699.8 (0.1)	125	2	50 228.3 (0.0)	129	3	50 255.0 (−0.2)
148	1	51 754.5 (0.3)	126	2	50 287.8 (−0.3)	130	3	50 314.0 (0.0)
149	1	51 808.5 (0.0)	127	2	50 347.5 (0.0)	131	3	50 372.1 (−0.5)
150	1	51 862.3 (−0.3)	128	2	50 406.7 (−0.3)	132	3	50 430.8 (−0.1)

^a Values in parentheses are observed — calculated residuals.

smaller than those of the ground state, and the excitation peaks will be red degraded. In fact, the difference in the rotational constants is sufficiently large that the vibronic bands do not possess a "conventional" bandhead, i.e., the $R(0)$ line is the most violet in the rotational contour.¹² We therefore feel it is justifiable to equate the band origin to the leading edge of the vibronic band profile. Using the molecular constants reported by Ishiwata *et al.*¹² which are valid up to $v' = 124$, an initial set of vibrational term values were calculated. From these and term values for the ground state, calculated from the constants reported by LeRoy,²¹ transition energies were predicted and compared with the observed values. In addition to this data set the vibrational levels from $v' = 52$ to 140 in the D state have been followed by optical-optical double-resonance measurements in our laboratory.¹³ These data, together with the single-photon data, allow an unambiguous assignment of the vibrational levels of the excited D state.

Figure 4 shows an excitation spectrum recorded using the sixth anti-Stokes line generated with the dyes QUI, DMQ, and PTP, with argon as the backing gas, which produces more efficient cooling than helium. The sample temperature was varied between 353 and 390 K, and the backing pressure was varied between 0.8 and 1.4 bar in order to optimize the fluorescence intensity. The spectrum is a composite of several scans necessitated by the realignment of the Raman-shifted output about every 500 cm^{-1} , as mentioned earlier. The major intensity variations in the spectrum are a result of this.

As the excitation energy increases, the Franck-Condon

factors for transitions from $v'' = 3, 2$, and 1 become lower relative to those for transitions from $v'' = 0$ until around 187 nm, where the spectrum is almost entirely due to bands arising from excitation from $v'' = 0$. This had been predicted by Tellinghuisen and Phillips,²² who also suggested that transitions from $v'' = 1$ and $v'' = 2$ should become significant again around 182 nm. However, excitation at these wavelengths was out of the range of the present experiments.

The vibrational term values, calculated from the constants reported by Ishiwata *et al.*,¹² were combined with the present set for $v' = 113$ to $v' = 210$ and least-squares fitted to the Dunham expansion

$$G(v') = \sum_i Y_{i,0} (v' + 1/2)^i$$

using a polynomial of degree six. The size of the polynomial expansion was chosen by successively increasing it until the extra parameters produced no further decrease in the standard deviation of the fit. The coefficients obtained are listed in Table II. In several previous studies⁵⁻¹⁰ the D state has been excited using the iodine atomic line at 183.0 nm. This has been shown to simultaneously pump five rovibronic levels of the D state, namely $v' = n, J' = 22$; $v' = n, J' = 25$; $v' = n + 1, J' = 46$; $v' = n + 1, J' = 49$; and $v' = n + 4, J' = 87$. Tellinghuisen¹⁰ proposed that n was 203 but that it could possibly be 204. We can confirm that n corresponds to $v' = 203$. The $G(v')$ values for $v' = 203, 204$, and 207 calculated using the present vibrational constants are between 1 and 2 cm^{-1} lower than those calculated from the energy levels and rotational constants given in Ref. 7. This may be

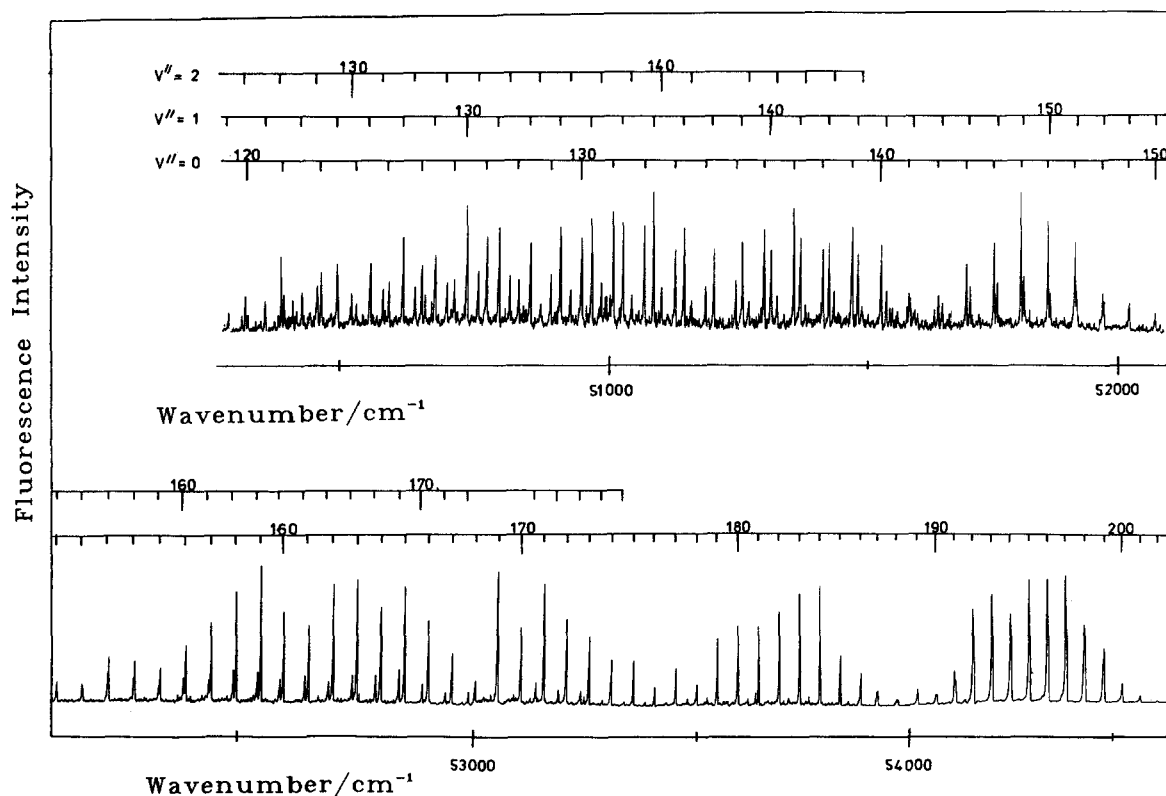


FIG. 4. $D \leftarrow X$ fluorescence excitation spectrum of jet-cooled I_2 recorded using the sixth anti-Stokes Raman-shifted output of QUI, DMQ, and PTP dyes and a backing pressure of 0.7 bar of argon. The intensity of the fluorescence was not normalized with respect to the laser power.

TABLE II. Vibrational constants for the *D* state of I₂.

Dunham parameter	Previous value ^a	Previous value ^b	Present value ^c
$Y_{0,0}$	41 028.584(47) ^d	41 026.4(4)	41 028.584(47)
$Y_{1,0}$	94.9928(60)	95.66(21)	95.0108(286)
$Y_{2,0}$	-0.109 19(26)	-0.1345(50)	-0.110 08(155)
$Y_{3,0}$	-5.805(50) × 10 ⁻⁴	-2.14(43) × 10 ⁻⁴	-5.759(310) × 10 ⁻⁴
$Y_{4,0}$	3.686(43) × 10 ⁻⁶	1.3(2) × 10 ⁻⁶	3.936(287) × 10 ⁻⁶
$Y_{5,0}$	-7.61(13) × 10 ⁻⁹	-1.7(2) × 10 ⁻⁹	-1.122(124) × 10 ⁻⁸
$Y_{6,0}$	1.367(204) × 10 ⁻¹¹

^aReference 12. Values are valid up to $v' = 124$.^bReference 8. Values are valid up to $v' = 260$.^cValues are valid up to $v' = 201$. Coefficients are quoted to higher precision than warranted by their standard deviations to avoid truncation error in the calculation of the vibrational term values given in Table I.^dValues in parentheses denote one standard deviation.

due in part to the extent to which our measurement of the leading edge of a vibronic band is a true measure of the band origin.

It has been suggested that a weak absorption from the ground state to a 1_u ion-pair state should appear between 181 and 184 nm,²³ but this has not been previously observed. We have populated the very lowest levels of this 1_u state in a perturbation-facilitated 1 + 1 OODR experiment and have determined that the strongest emission occurs at 350 nm, which we have assigned to a transition to a repulsive 1_g valence state.²⁴ It was not possible to collect fluorescence at 350 nm in these present single-photon experiments due to a large scattered light signal at this wavelength. Weaker emission from the same system will also occur at 322 nm; however, no bands which could be assigned to a 1_u-1_g transition were observed, and any such fluorescence must be at least ten times weaker than that of the *D-X* system.

By using higher-order anti-Stokes lines it should be possible to obtain spectra in the region between 170 and 185 nm, where some interesting features have been observed in the fluorescence excitation spectrum of room temperature I₂, obtained with synchrotron radiation.⁴ A series of dips have been observed in the *D-X* system which have been assigned to perturbations between the *D* state and isoenergetic levels of the C₆ Rydberg state. In addition, a weak system, seen in the region of 170 nm, has been assigned to the transition $F(O_u^+) \leftarrow X(O_g^+)$. Clearly, further work on jet-cooled I₂ in this shorter-wavelength region, at the resolution we have been able to achieve in the present study, would be desirable.

B. Spectra recorded at rovibronic resolution

We have recorded a few of the vibronic bands in the *D-X* fluorescence excitation spectrum at higher resolution. Spectra of the (194,0) band and of the overlapping (161,0) and (165,1) bands, recorded between 184.33 and 184.43 nm and between 189.90 and 190.00 nm, respectively, are shown in Figs. 5(a) and 5(b). Only mild expansion conditions (backing pressure 0.4 bar, which provided a rotational temperature of ~15 K) were used in order to observe a wide range of rotational features. The spectra appear well resolved because the $R(J)$ and $P(J-1)$ lines are separated by only 0.02 cm⁻¹ and are effectively coincidental at our reso-

lution (~0.3 cm⁻¹). As lower v' levels are accessed the separation between these pairs of lines increases, thus broadening the observed features and making an accurate rotational analysis difficult.

Assuming that $R(J)$ and $P(J-1)$ lines are coincident, B_v values were calculated by least-squares fitting the positions of the $R(J)$ rotational lines to the expression

$$B' = (\tilde{\nu}_{\text{expt}} + B''J^2)/(J^2 + 2),$$

where $\tilde{\nu}_{\text{expt}}$ is the observed wave number of the rotational line, and B' and B'' are the upper- and lower-state rotational constants. Transitions involving rotational levels up to $J = 35$ were used in the fit for the (194,0) band, only those

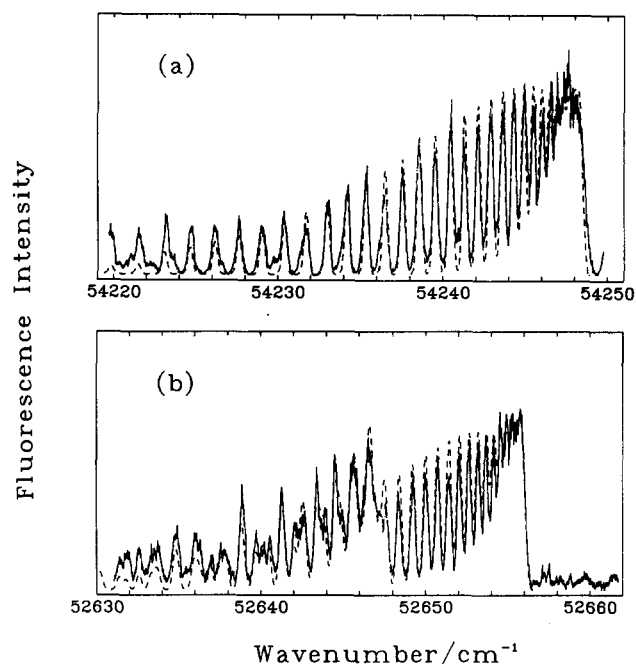


FIG. 5. *D-X* fluorescence excitation spectrum of the (a) (194,0) and (b) (165,1) and (161,0) bands of jet-cooled I₂ recorded with a backing pressure of 0.4 bar of helium. The solid line shows the experimental spectra and the dashed line the simulated spectra. [In the simulations B_v values of 0.012 50, 0.013 58, and 0.013 73 cm⁻¹ were used for $v' = 194$, 165, and 161, respectively, and the bandwidth was 0.34 cm⁻¹. Relative intensities of the overlapped bands (161,0) and (165,1) were scaled to match the experimental spectrum.]

up to $J = 19$ were used for the (161,0) band, since to lower wave number it is overlapped by the (165,1) band. In this way B_v values for the $v' = 161$ and $v' = 194$ levels of the D state were obtained, 0.013 73(34) and 0.012 495(60) cm^{-1} , respectively. (Simulated spectra using these constants are shown for comparison in Fig. 5.) The rotational constants quoted by Tellinghuisen⁸ generate B_v values of 0.013 668 and 0.012 455 cm^{-1} for these vibrational levels, which lie within our error limits.

IV. CONCLUSION

We have successfully recorded the one-photon fluorescence excitation spectrum of jet-cooled I_2 down to 184 nm, at high resolution using the fifth and sixth anti-Stokes Raman-shifted output from an excimer pumped dye laser. Within the accuracy of our measurements ($\sim 0.5 \text{ cm}^{-1}$) there is no sign of any perturbation in the vibrational levels of the $D(O_u^+)$ state. This observation is supported by Hoy and Brand,²⁵ who have studied the $F(O_u^+)$ state of I_2 using a 1 + 2 multiphoton ionization technique. They concluded that perturbations which they detected in low vibrational levels of the $F(O_u^+)$ state were not due to interaction with the $D(O_u^+)$ state. This contrasts with results from studies on the one-photon fluorescence excitation of the $D(O_u^+)$ state of jet-cooled bromine,^{26,27} where the observed vibrational levels differed from the calculated levels by up to 7 cm^{-1} . There, the perturbations were assigned to a homogeneous interaction between the $D(O_u^+)$ and $F(O_u^+)$ states.

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